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Interim Report
I-A2172-3

RELATIONSHIP BETWEEN PROPELLANT COMPOSITION AND FLASH AND SMOKE PRODUCED BY COMBUSTION PRODUCTS

by

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March 14 to September 13, 1955

Prepared for

AMMUNITION BRANCH

Research and Development Division
Office, Chief of Ordnance, U.S. Army
Contract DA-36-034-501-ORD-78RD
Project TA1-360

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ABSTRACT

The ignition limits of mixtures of muzzle gas and air are being measured with a shock tube as part of a study of gun muzzle flash. The muzzle gas is simulated by mixing its components in the proportions of the calculated propellant combustion products. A few changes and additions have been made to the apparatus used in this work. Acquisition of a counter-chronograph has made it possible to simplify the procedure for measuring shock velocity. A spark source and associated delay circuit, previously used in photography of gun firing phenomena, have been repaired and rebuilt in preparation for spark photography of shock tube phenomena. Two conditions that can cause misinterpretation of shock tube observations have been encountered. It has been found that radiation from particles of shock tube diaphragm material, heated by the hot gas behind the reflected shock wave, can give the impression that the gas itself has ignited even in cases where no gas ignition occurs. This is particularly true for Kodatrace diaphragms. Using a non-combustible gas in the shock tube, we have determined the approximate requirements on pressure, temperature, and oxygen concentration in the gas surrounding the diaphragm particles for radiation to be observed. Another condition that can cause misleading results is the development of "hot" spots at the end face of the shock tube where shock reflection occurs. In our experiments these hot spots appeared to originate in crevices that formed along the edges of a gasket used in sealing the end face. We have eliminated data that had been affected by the above two conditions.

Determination of ignition boundaries for mixtures of M2 muzzle gas and air and M17 muzzle gas and air at pressures between one and five atmospheres have been completed. In the case of the M17 muzzle gas, previously published data had to be corrected by consideration of the two conditions discussed above. Generally, the mixtures exhibit an increase in minimum ignition temperature with pressure, which is indicative of a chain-branching mechanism.

The shock tube has also been used to determine the ignition boundaries at one atmosphere for wet and dry mixtures of carbon monoxide and air. Addition of water vapor to mixtures containing less than approximately 25% air, by volume, caused a drop in minimum ignition temperature. Mixtures in which the water vapor was replaced by nitrogen had the same ignition limits as the dry mixtures of carbon monoxide and air (without nitrogen). Hence, the effect of water vapor appears to be a chemical, rather than a physical, one. Since the combustion of carbon monoxide is known to be strongly affected by the presence of small quantities of hydrogen and/or water vapor chromatographic techniques are being developed for the determination of traces of these gases in the dry experimental

gas. The gas chromatography apparatus and a special technique for determination of water vapor, involving conversion to acetylene in a column of calcium carbide, are described.

The results of a literature study on obscuration by smokes is presented. Scattering theory, contrast ratio, optical density and the influence of field conditions are discussed. Obscuration by smoke is shown to be a complex phenomenon whose thorough study includes detailed investigation of the physical properties of the smoke cloud and its component particles.

Smoke tests have been made on salted M1 (1.0% K_2SO_4) and unsalted and salted (0.3% cryolite) T34 propellants using a Caliber 0.50 machine gun and special artillery type copper banded projectiles. The unsalted T34 propellant had the least dense smoke. Compared to this, the density of smoke from the salted T34 propellant was about 50% higher and that of the salted M1 propellant was about twice as dense. All three propellants were relatively flashless.

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INTRODUCTION

This report covers the accomplishments of the latest six month period in a long range program, whose scope has varied from time to time, but which has been concerned mainly with the study of problems related to prevention of the flash and smoke produced on firing guns. Over the years there have been both theoretical and experimental studies of some of the fundamental processes occurring in the production and suppression of gun muzzle flash along with empirical studies of flash suppression with mechanical devices and propellant additives. Work on the smoke problem has included the collection of data on the chemical composition and optical density of gun smoke. Reference (1)* provides a convenient summary of earlier work, and References (2) and (3) cover the work done during the periods immediately preceding that covered in the present report.

1. SHOCK TUBE DETERMINATIONS OF IGNITION LIMITS OF MIXTURES OF MUZZLE GAS AND AIR

1.1 Motivation and General Aspects of Investigation

The products of propellant combustion emerge from the muzzle and mix with the surrounding air when a gun is fired. Small volume elements of gas outside the gun will range in composition from 100% muzzle gas to 100% air, and they will have pressure and temperature distributions governed by the internal ballistics and the external gas dynamics. If the time history of composition, pressure, and temperature of one of the gas elements satisfies the requirements for ignition a flame will be initiated. The phenomenon of gun flash results when the conditions are suitable for the flame to be propagated throughout the remainder of the muzzle gas-air mixture. There are thus two categories of information involved in a knowledge of muzzle flash: one is concerned with the physical state of the gases outside the gun, and the other is concerned with the requirements for ignition. One can expect muzzle flash to occur whenever these

*References are indicated by underscored numerals in parentheses

two sets of conditions overlap. Both of these categories are being studied with the object of arriving at basic requirements for preventing flash.

The determination of the physical state of the gas mixture outside the gun under steady flow conditions has been approached on a theoretical basis. The first effort(4) in this line assumed that the mixing of air and muzzle gas occurs entirely at atmospheric pressure; and a later extension(3) of the mathematical development took into account the presence of the normal shock wave in front of the muzzle. Equations are now available for calculating the temperature of the muzzle gas-air mixtures as a function of air concentration for each of the following cases:

A. The muzzle gas expands to atmoshperic pressure, then mixes with air at atmospheric pressure.

B. (An extension of Case A) After the muzzle gas and air have mixed at atmospheric pressure, the mixture passes through a shock wave and then expands to atmospheric pressure.

C. The muzzle gas expands to atmospheric pressure, passes through a shock wave, and again expands to atmospheric pressure before mixing with air at the same pressure.

Calculations have been made for all three cases for the 37 mm Vigilante weapon using T28 propellant(3). Although this work has not been carried beyond the stage recorded in Reference (3), further developments of the theory and calculations for other weapons are planned for the near future.

The second category, that concerned with the requirements for ignition, has been approached primarily on an experimental basis. The current effort involves the determination of the ignition boundaries of mixtures of muzzle gas and air, at pressures up to five atmospheres, using a shock tube. In this work the muzzle gas is simulated by a mixture of its components in concentrations corresponding to the calculated combustion products of the given propellant. The mixture of dry ingredients is

obtained from a supplier in a commercial gas cylinder and the water vapor is added separately. (The amount of water vapor added accounts both for that present in muzzle gas and that in an atmosphere of typical humidity: 51% relative humidity at 20.5°C.) The gas mixture is heated and compressed in the shock tube by propagation of both the incident and reflected shock waves. A measurement of the incident shock speed is used in determining the pressure and temperature of the mixture after it has been crossed by the two shock waves; and a photomultiplier is used to detect ignition. The ideal theory of the shock tube is assumed to hold, even though it is recognized that the actual shock tube behavior involves many non-ideal conditions. Although the absolute values of pressure and temperature may differ from those calculated on the basis of the ideal theory, our examination of the non-ideal effects indicates that the relative effects of changes in gas composition are exhibited correctly. Details of apparatus, experimental procedure, and non-ideal effects have been discussed in earlier reports (1, 2, 5).

1.2 Apparatus, Modifications and Additions

A major improvement was made in the method of determining shock wave velocities by the incorporation of an electronic counter chronograph (Potter Instrument Co., Inc., Model 450) into our experimental apparatus. In the past, shock wave velocities were determined by the time-consuming procedure of measuring, from a photograph of a raster exhibited on an oscilloscope screen, the time interval between two electronic pulses produced as the wave traversed a known distance in the shock tube. These pulses were produced by the incident shock wave as it was detected by (a) a schlieren-phototube system and (b) a piezoelectric detector at the end of the shock tube. In our new system the time interval is measured automatically to within 0.625 μsec by the chronograph counter as it is started and stopped by the pulses (a) and (b), respectively.

A number of experiments were performed to compare the time for given shock waves to traverse the distance between detectors as registered

automatically by the counter and as measured by the former oscillographic method. The differences Δt, between the times obtained by the two methods, are recorded in Table 1. The average difference was found to be approximately 2 microseconds, which amounts to less than 0.2% of the total time interval.

Table 1

COMPARISON OF SHOCK WAVE TRAVEL TIMES AS MEASURED BY TWO TECHNIQUES

Experiment No.	t (msec) Oscillographic Method	t (msec) Registered by Counter	Δt (μsec)
1212	1.1886	1.1875	1.1
1213	1.1993	1.1981	1.2
1214	1.2023	1.2000	2.3
1215	1.1684	1.1656	2.8
1216	1.1225	1.2000	2.5
1217	1.0846	1.0806	4.0
1218	1.0863	1.0850	1.3
1219	1.0444	1.0425	1.9
1220	1.0839	1.0831	0.8

Equipment for shadowgraph photography, previously used on this project in firing tests, has been repaired and improved in preparation for use in shock tube work. A spark source has been largely rebuilt. A time delay circuit has been slightly modified so that it can be activated by a thyratron pulse, and it has also been recalibrated. This equipment, which had not been used for a few years, is now in operating order and is available for photography of shock tube phenomena. It will be used in conjunction with a rectangular cross-section shock tube which we plan to build in the near future. The objective will be to examine the real behavior of the shock tube; and, among other things, to acquire a better estimate of the extent to which our experimental observations are influenced by non-ideal effects. This work cannot readily be carried out with the present circular cross-section shock tube. Although it is possible to photograph phenomena by shadowgraph and schlieren techniques through

narrow slits parallel to the axis of a cylindrical tube it is impractical to obtain shadowgraphs or schlieren pictures of the entire cross-section because of interference effects caused by the curved walls through which the light must pass.

1.3 Shock Tube Diaphragm Experiments

During the course of shock tube experiments at pressures above one atmosphere it was discovered that, occasionally, radiation fell on the photomultipler detector even when we were quite certain that the temperature was too low for the gas itself to have produced radiation either by ignition or ionization. An investigation revealed that the radiation came from particles of the shock tube diaphragm heated by the hot gas behind the shock wave. It was found that the effect is dependent upon the diaphragm material and the temperature, pressure, and oxygen content of the gas surrounding the diaphragm particles. An exhaustive study was not made, but enough experiments were performed to determine approximately the range of conditions under which radiation might be expected without gas ignition. It was found that neither clear cellophane, nor red "Zip" tape radiate appreciably when the shock tube is filled with air (which results in a greater oxygen concentration than in normal experiments) at temperatures up to 1200°K and pressures up to five atmospheres. Since this covers the entire range of our experiments it is possible to avoid the above difficulty by using either of these two diaphragm materials. However, it is inconvenient to use them at the higher pressures where their strength limitations requires that as many as six layers be used as a diaphragm. From the strength standpoint we had found it more convenient to use Kodatrace diaphragms at higher pressures. This material, however, produces the unwanted radiation. Figure 1 indicates approximately the conditions of pressure, temperature, and oxygen concentration which cause the Kodatrace diaphragm particles to glow.

WHEN THE PRESSURE AND TEMPERATURE OF THE GAS SURROUNDING THE DIAPHRAGM PARTICLES FELL ON POINTS TO THE RIGHT OF THE BOUNDARY, THE PARTICLES WERE OBSERVED TO GLOW, PRODUCING A PHOTOMULTIPLIER SIGNAL WHICH COULD BE MISINTERPRETED AS RESULTING FROM GAS IGNITION. THE BOUNDARY MOVES AWAY FROM THE ORIGIN AS THE VOLUME CONCENTRATION OF OXYGEN IN THE GAS DECREASES.

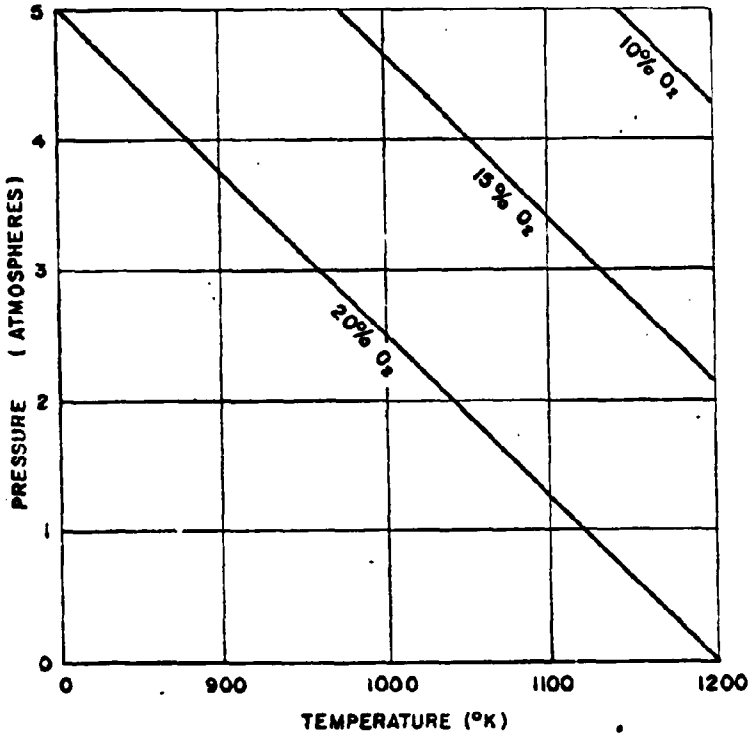

FIGURE I. CONDITIONS UNDER WHICH KODATRACE DIAPHRAGMS PRODUCE RADIATION

Mylar film provides a relatively strong diaphragm material; however, we encountered difficulty in rupturing it satisfactorily. We found that, when the pressure difference across the diaphragm was within a small range of values below that which caused spontaneous rupture weakening the diaphragm by piercing it with a plunger frequently caused it to split along a single line only - so that the cross-section of the shock tube remained partly blocked. At somewhat lower pressure differences, the weakening effect of the plunger was so small that the diaphragm did not rupture at all. A four-edged plunger, which produced a cross cut in the diaphragm, was constructed and tried with the intention of causing splitting along at least two lines. No significant improvement was achieved, however.

1.4 Ignition Boundaries of Mixtures of Muzzle Gas and Air

The ignition boundaries for five different mixtures of M17 muzzle gas and air were given in Figure 1 of Reference (3). The data from which the boundaries were drawn included occasional experiments in which the observed ignition delay appeared to be too long, or too short, by comparison with other experiments within a group. As will be described below we have succeeded in finding the probable causes of these abnormal results, and have eliminated them from our data. By this means and by obtaining new data, where necessary, we have corrected the boundaries and have redrawn them in Figure 2 of this report.

The basis for eliminating long delays is the following: Under normal conditions we observe whether or not the experimental gas ignites while it is in the pressure-temperature state (designated State 5 in previous reports) that exists behind the reflected shock wave. The experimental gas remains in this state until it is changed by the passage of an expansion wave, generated by the interaction of the reflected shock wave with the contact surface (see Reference (1), p. 32). The small decreases in pressure and temperature caused by the expansion wave tend to inhibit ignition and lengthen the induction period.

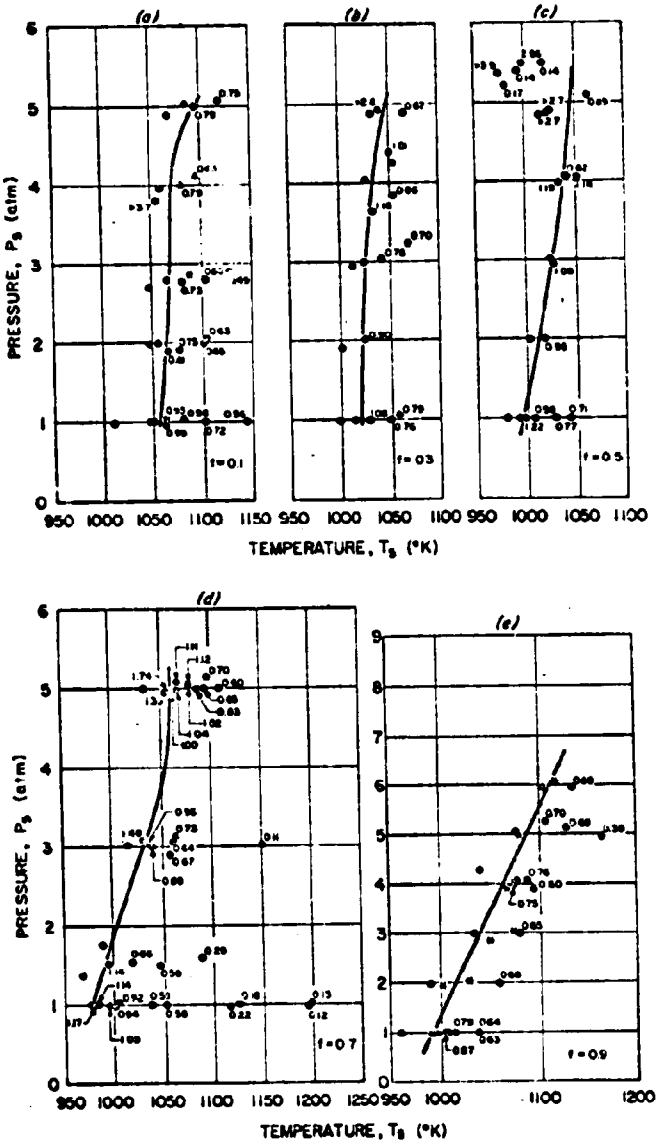

FIGURE 2. IGNITION BOUNDARIES FOR MIXTURES OF M17 MUZZLE GAS AND AIR

Numerals indicate ignition delays in milliseconds.

Points without numerals represent experiments in which ignition did not occur.

- ▫ Very low radiation emitted.
- Δ Low radiation emitted during ignition delay, then sudden increase in radiation emitted.
- f Volume fraction of air in mixture.

Such cases are indicated by the fact that the observed ignition delay exceeds the calculated maximum duration of State 5. Because of the change of state during the induction period, experiments found to fall in this category were disregarded in determining the location of the corrected ignition boundaries.

The occurrence of abnormally short ignition delays appears to have resulted from the production of hot spots at the back face of the shock tube. These hot spots are believed to have occurred at crevices that developed, between a rubber gasket and brass plug, due to changes in dimensions of the gasket after repeated use. Under otherwise identical conditions unexpectedly short ignition delays ceased to occur when the crevices were eliminated either by cementing the gasket or by replacing it. Experiments that appeared to have been influenced by hot spots were also eliminated from our data.

The above corrections were required mainly at the higher pressures; and their chief effect was to erase the apparent decrease in ignition limit that had been observed for some of the muzzle gas-air mixtures at pressures above four atmospheres. The corrected boundaries generally exhibit an increase of ignition limit temperature with increase in pressure. The same data that were used in drawing the curves in Figure 2 have been used to draw the constant pressure ignition boundaries shown in Figure 3. Each curve, for the pressure indicated gives the minimum ignition temperature as a function of the mass fraction of air mixed with the M17 muzzle gas.

Ignition boundaries have also been obtained for mixtures of air and M2 muzzle gases. The constant pressure boundaries at 1, 3, and 5 atmospheres are shown in Figure 4. Note that, with the exception of the results for the mixture containing 10% air by mass ($r = 0.1$), the minimum ignition temperature for a given composition increases with pressure.

According to combustion theory the tendency of the minimum ignition temperature to increase with pressure is attributable to a

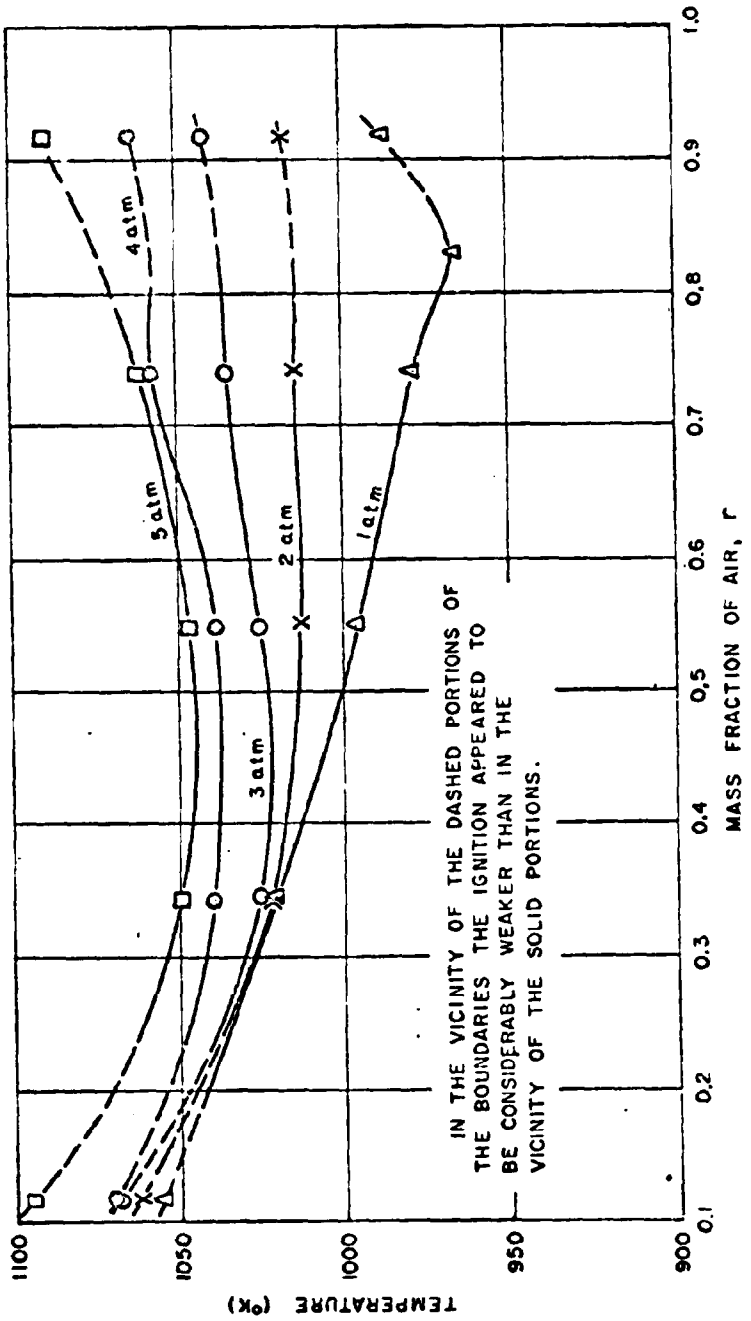

FIGURE 3. IGNITION BOUNDARIES FOR MIXTURES OF M17 MUZZLE GAS AND AIR AT PRESSURES FROM 1 TO 5 ATMOSPHERES

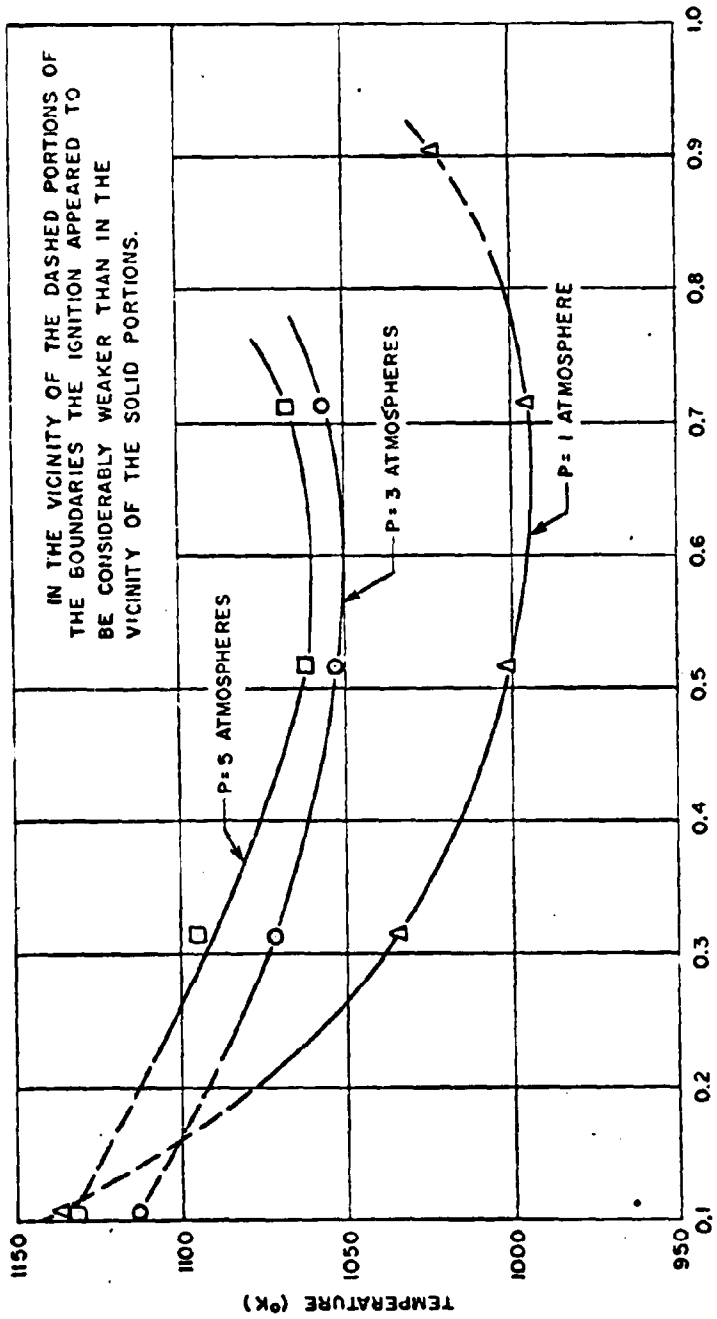

FIGURE 4. IGNITION BOUNDARIES FOR MIXTURES OF M2 MUZZLE GAS AND AIR AT PRESSURES OF 1, 3 AND 5 ATMOSPHERES

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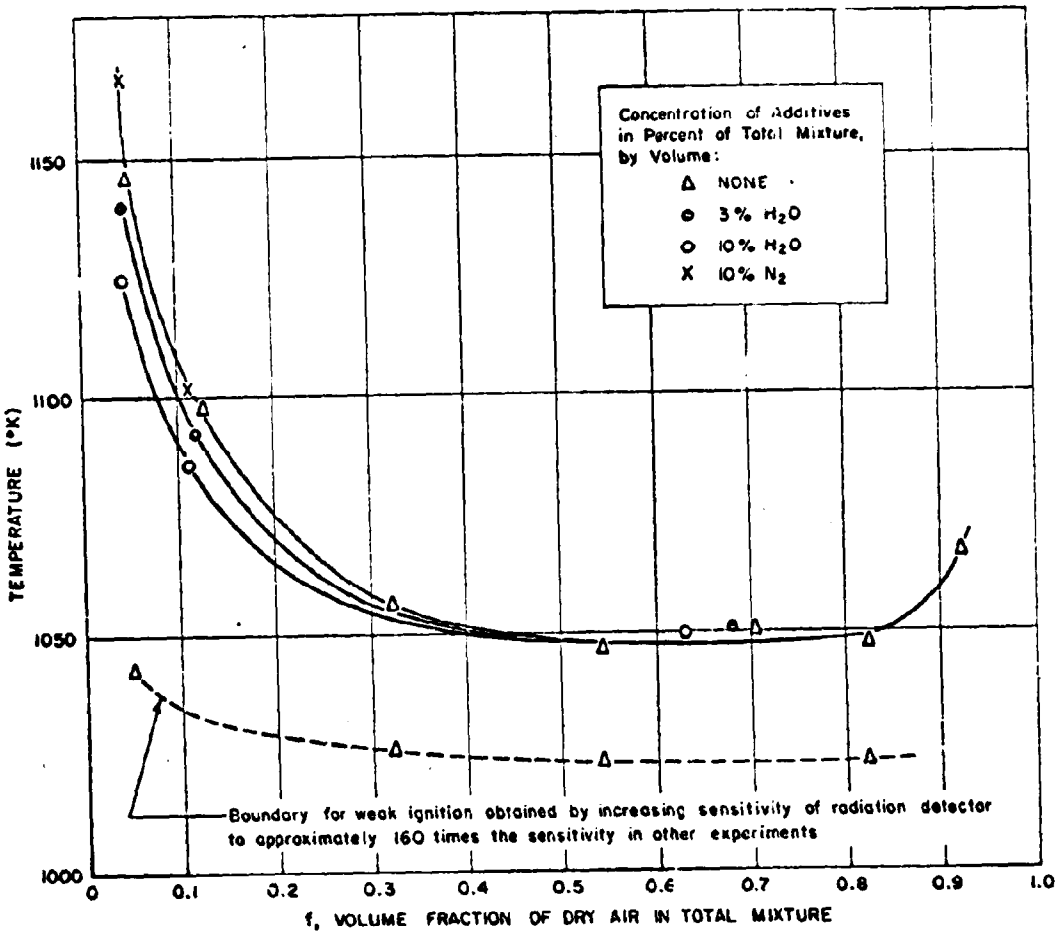
chain-branching mechanism where increasing pressure results in increased chain-breaking by collision in the gas phase. Thermal ignitions, on the other hand, are characterized by decreasing ignition temperatures with increasing pressure since the energy produced by reaction is absorbed by neighboring molecules or atoms, inducing their participation in the reaction.

Experiments are now in progress with mixturesof M10 muzzle gas and air. In preparation for future work we have ordered a gas mixture simulating M6 muzzle gas.

2. IGNITION LIMITS OF DRY AND WET MIXTURES OF CARBON MONOXIDE AND AIR

A study of the CO-Air-H_2O-H_2 system has been initiated with the aim of increasing our understanding of the muzzle gas-air reaction. This work is being carried out at a relatively low rate of effort concurrently with the muzzle gas studies, using the same equipment and experimental procedures. The relative simplicity of the CO-Air system, with small amounts of H_2O and/or H_2 added - as compared to the complex muzzle gas-air system - should facilitate the interpretation of our data in terms of fundamental reaction processes. So far we have obtained the ignition limits at atmospheric pressure of both dry and wet mixtures of CO and air.

The results of experiments are shown in Figure 5, where the minimum ignition temperature is plotted against the volume fraction of air in the mixtures studied. The upright triangles represent the data obtained with dry mixtures of CO and air. The stoichiometric mixture is represented by f = 0.704. In the experiments used to draw the dashed line boundary the sensitivity of the radiation detector was increased to approximately 160 times the sensitivity normally used. These high sensitivity experiments disclosed that very weak ignitions occur at temperatures below the ignition limits determined with the radiation detection sensitivity set at the value used in all our other experiments. The ignition temperature for these relatively weak ignitions is seen to be



FIGURES 5. IGNITION BOUNDARIES FOR MIXTURES OF CARBON MONOXIDE AND AIR AT ONE ATMOSPHERE

relatively independent of composition, except in the region where the air content becomes so small that the amount of reaction occurring is relatively insignificant. For the stronger ignitions (solid line boundary) there was a pronounced increase in minimum ignition temperature when the air concentration was reduced to low values.

To check the effect of adding water vapor to the mixtures experiments were run with 3% and 10% H_2O, by volume, added to several dry mixtures. In each set of experiments the ratio of air to CO in the dry mixture was kept constant, and the water concentration is stated as a percent of the total mixture. This had the effect of reducing the value of f, the volume fraction of dry air in the total mixture. For example, when 3% and 10% H_2O were added to the stoichiometric, dry mixture the value of f was decreased from 0.704 to 0.683 and 0.634, respectively.

Reference to Figure 5 shows that adding up to 10% of water vapor did not affect the ignition temperature of the stoichiometric mixture. When added to mixtures with low air concentration, however, water vapor caused the ignition temperature to decrease by amounts which increased with water concentration.

Since it was found that the introduction of small amounts of water vapor produced a lowering of the ignition temperature, an attempt was made to remove any residual water vapor in the gases employed in our experiments. The object of this test was to see if any further increase in the minimum ignition temperature could be obtained. Thus the tank CO and tank air normally used in our experiments were passed slowly through two 1 in. diameter tubes, 4 ft long, containing magnesium perchlorate drying agent. The emerging gases were then utilized to repeat previous experiments. It was found that no discernible changes occurred in the minimum ignition temperatures previously found using gases directly from the tanks. These results indicated that further removal of water from the tank gases produces no significant change in the ignition limits. It is realized, of course, that the trace amounts of water left in the tank gases after drying with $MgClO_4$ may have a large effect on the

ignitability of CO-air mixtures. Attempts will be made shortly to determine the quantity of water vapor in the tank gases by chromatography.

In an effort to ascertain whether added H_2O vapor played a physical or chemical role in reducing the ignition temperature, 10% N_2, by volume, was added to the CO-air mixture. It was found that introducing this amount of N_2, equivalent to the quantity of H_2O vapor used in our previously described experiments, produced no effect on the ignition temperature. Thus the lowering of the boundary by H_2O vapor addition does not appear to be due to removal of a quantity of reactants or an inert-body effect, but to an alteration in the chemical mechanism.

3 CHROMATOGRAPHIC ANALYSIS FOR HYDROGEN AND WATER VAPOR

The literature on carbon monoxide combustion indicates that ignition is strongly influenced by the presence of small amounts of hydrogen and/or water vapor (6, 7, 8). We have been interested, therefore, in determining whether our (dry) CO-air mixtures contain trace amounts of H_2O and H_2 in high enough concentration to influence the reaction. Water vapor and hydrogen might enter our gas mixture through one or more of the following sources: Impurities in the gases themselves (as supplied in commercial cylinders), by leakage of room air into the shock tube, and out-gassing of the walls of the shock tube and the flask in which the gases are premixed. Although we are really interested in the impurities present in the experimental gas mixture in the shock tube, our initial checks have been made on the CO and air in the supply tanks.

Gas chromatography, which is now widely used for gas analysis, is the method we have employed for detection of both hydrogen and water vapor, the latter requiring a preliminary conversion to acetylene before detection. Apparatus which was available in our laboratories was modified and improved before use in the above work. Figure 6 is a diagram of the essential parts of the apparatus. The detector is a thermal conductivity cell containing electrically heated wire filaments which are connected in a bridge circuit. The carrier gas is made to flow at a constant rate

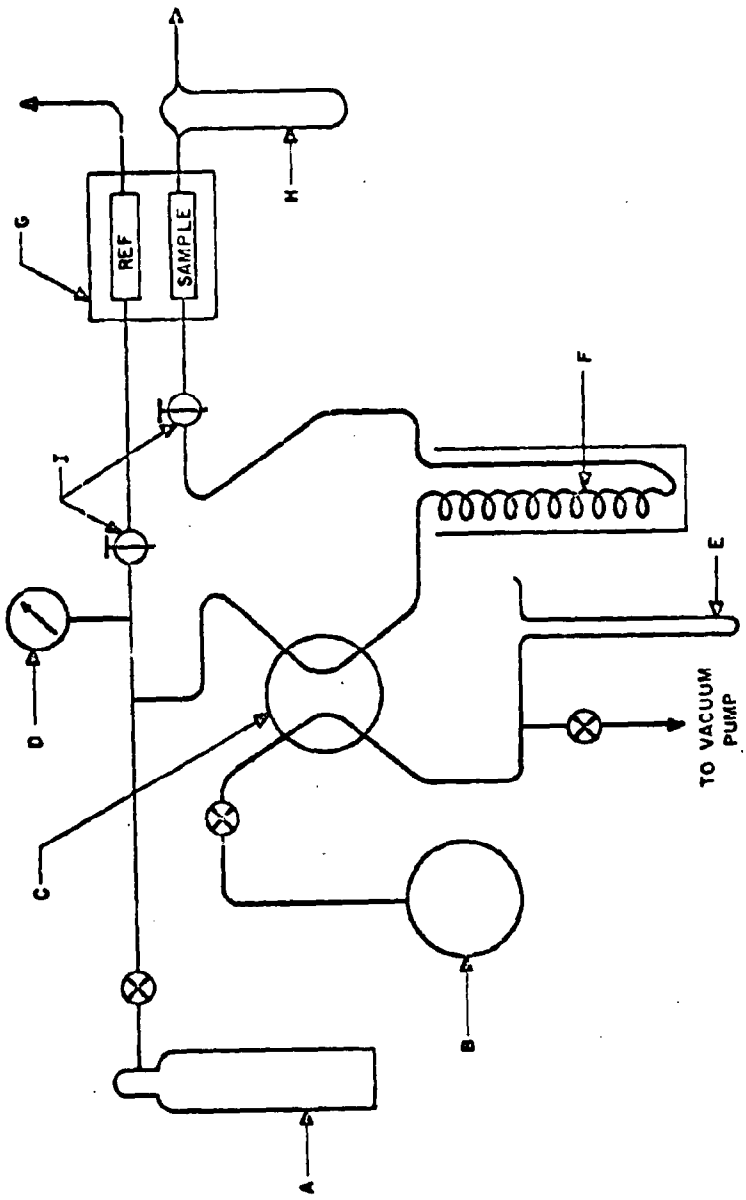


FIGURE 6. FLOW SCHEMATIC OF GAS CHROMATOGRAPHY APPARATUS

over the filaments in the reference side of the cell, and the carrier gas mixed with components of the gas being analyzed flows over the filaments in the sample side of the cell. The bridge is balanced with the carrier gas flowing through both sides of the cell. In operation, the presence of components of sample gas in the sample stream changes its thermal conductivity and causes changes in filament resistance. This results in a bridge unbalance which is registered on a recorder. The quantity of gas represented by the output signal is determined by calibration with known sample gases. In order to identify the components of the sample it is necessary to separate them and this is accomplished by elution of the sample through a suitable column. A 12 ft length of coiled 1/4 inch diameter copper tubing packed with Linde 5A molecular sieve and argon carrier gas were used for detection of hydrogen. A similar coil packed with a fine mesh of dimethylsulfolane and helium carrier gas were used for detection of acetylene in the tests for traces of water vapor as described further below. Figure 6 shows a sampling valve which in one position allows a trap to be filled with sample gas and in the other position allows the carrier gas to convey the trapped gas to the separating column. Each component of the sample progresses through the column at a rate depending upon its affinity and the rate of carrier gas flow. The differences in elution times provides the means of separating and identifying the various components of the gas sample.

Application of the above technique for the detection of hydrogen in our carbon monoxide and air supplies indicated that these gases contained the order of 10 ppm of hydrogen. This is simply an order of magnitude figure because at such low concentrations the limit of sensitivity is approached.

A chromatographic technique is presently being developed to determine very small quantities of water vapor. This technique employs our existing chromatography apparatus, modified slightly by inserting a 3 ft length of 1/4 in. diameter plastic tubing containing pulverized calcium carbide in the gas line. Gaseous samples, which are placed into

the helium stream of the chromatograph, pass through the CaC_2 before entering the main separating column. Any water vapor in the sample is absorbed by the CaC_2 and reacts with this material to produce acetylene. The acetylene passes into the main dimethylsulfolane column where it is eluted approximately seven minutes later, using our present flow rates. The amount of acetylene produced is determined by referring to a calibration curve constructed by plotting conductivity cell output versus known acetylene concentrations. Finally the original amount of H_2O vapor in the sample is obtained by merely doubling the determined acetylene concentration [$2H_2O + CaC_2 \rightarrow C_2H_2 + Ca(OH)_2$]. We plan to use this technique to analyze gaseous samples obtained from the shock tube itself.

4. STUDIES OF GUN SMOKE

Investigation of the gun smoke problem was undertaken with the aim of bettering our understanding of the causes of gun smoke and the means of eliminating it. The experimental program has included the testing of various propellants in a firing range using a caliber .50, M2 Browning machine gun with a 36 in. barrel as the test vehicle. Smoke samples were collected and used for chemical analysis and to determine the relative quantities of smoke produced by different propellants. A relative measure of optical density of the smoke was also made. References (2) and (3) describe the apparatus and procedures that were developed for the above tests. Reference (3) presents the results of tests on approximately ten propellant samples. During the period covered by this report three additional propellant samples were tested with the results reported below in Section 4.2. In addition, a literature investigation of the general problem of obscuration by smoke was made, and this information is presented below in Section 4.1.

4.1 Obscuration by Smokes

If light travelling from an object to an observer passes through a cloud of smoke some of the light will be scattered by the particles of

smoke. This decreases the quantity of light reaching the observer and also reduces the contrast between the object and its background. These effects tend to obscure the object. We present below some of the theory involved in light scattering and obscuration by smokes.

The scattering of light by molecules or particles in the atmosphere is not a simple phenomenon. Its intensity is dependent on the size of the scattering particles, their index of refraction, the wavelength of the incident light and the angle of observation in relation to the incident beam. It accounts for several well known phenomena: the blue of the sky, red sunsets, the diffusion of sunlight around us, the obscuration of distant objects by haze and many others. As yet no simple analysis of scattering has been made. If the scattering particles are of various sizes and indices of refraction, if the incident light is heterochromatic, it is an extremely difficult, if not an impossible matter, to predict the intensity of the scattered light in any given direction.

There are two well known theories of the scattering of light by particles. The first of these, due to Rayleigh, applies only to very small spherical particles, i.e. to those of diameter much smaller than the wavelength of the incident light. The second theory, that developed by Mie, is more generally applicable, not only to very small spherical particles but also to larger ones (ranging from 0.1 to 10μ) such as those present in smokes and clouds. The following summary of these theories and of the equations derived, is based on the presentation given in Reference (9).

The Rayleigh equations of scattering are comparatively simple. For one particle the intensity of scattered light is given by

$$I_\theta = \frac{9\pi^2 V^2}{2R^2\lambda^4}\left(\frac{m^2-1}{m^2+4}\right)^2 (1+\cos^2\theta) \qquad (1)$$

where I_θ = the intensity of the scattered light in the direction θ

θ = angle of observation relative to the incident beam

V = the volume of the particles

R = distance of point of observation from the particle

m = index of refraction of the particle relative to the medium in which the particle is suspended.

λ = the wavelength of the light incident on the particle

The intensity of the incident beam is taken as equal to unity.

The total intensity of the scattered light S, when unit energy of illumination falls on unit area, calculated from Equation (1), is given by

$$S = 24\pi^3 \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 \frac{V^2}{\lambda^4} \qquad (2)$$

For large particles the Mie equations, rather than the Rayleigh equations are applicable. In these equations the angular scattering intensity I_θ is given by

$$I_\theta = \frac{\lambda^2}{8\pi^2 R^2} \left(i_1 + i_2 \right) \qquad (3)$$

The values of i_1 and i_2 are functions of the coefficients of the amplitudes of the electric and magnetic components of the light waves, a_n and b_n, respectively, and result in a complicated series of terms involving Bessel, Hankel and Langendre functions and the parameters α and m where $\alpha = 2\pi r/\lambda$, r being the radius of the particle and m the index of refraction, as above.

The total scattering by one particle for unit incident intensity is given by

$$S = \frac{\lambda^2}{2\pi} \sum_{n=1}^{\infty} (2n+1)\left(|a_n|^2 + |b_n|^2 \right) \qquad (4)$$

These equations show that the angular distribution of the intensity of scattered light is an extremely complicated function of the

various parameters involved, especially the particle size and the index of refraction.

Plots of I_θ for various particle sizes and indices of refraction, given in Reference (9) illustrate the complexity of this problem. These curves show the tremendous changes that occur in the functions i_1 and i_2 as α and m are increased. These changes do not depend in a regular way on the angle of observation, although the scattering is always a maximum when θ is 180°. Nor does the percent scattered in any given direction vary with discernible regularity as the particle size increases or the index of refraction is varied.

In these calculations a "total scattering coefficient" K_S, is found to be convenient. This coefficient is defined as the ratio of the apparent cross-sectional area of a particle to the geometrical cross-sectional area, and is given by

$$K_S = \frac{S}{\pi r^2} \tag{5}$$

where S has the value in equation (4).

A plot of K_S versus α in Reference (9) exhibits several maxima and minima as the particle size is increased. The exact value of K_S depends not only on the particle size but on its index of refraction as well.

The Mie equation may be approximated over a small range of values of the radius of the particle for any given wavelength and index of refraction, as follows:

$$I_\theta = kr^p n \tag{6}$$

where r^p = the particle radius raised to some power p

n = the number of particles per unit volume

k = a constant

I_θ = the intensity of light scattered in a given direction from a given volume of aerosol

A plot of p versus r at $\theta = 45°$, $m = 1.44$, depicted in Reference (9) shows that p decreases from 6 to -1 as r varies from approximately 0.1μ to 0.3μ and then increases to approximately 5 with a further increase in the particle size. Increasing the index of refraction to 1.55 does not alter the value of K_S greatly except at larger particle sizes where a second minimum appears.

From the above brief summary of the theory of scattering of light by spherical particles and of the equations which have been derived, it may be concluded that unless the particle size, the index of refraction of the particles and the total number of particles are known, it is impossible to make any accurate predictions as to the intensity of the scattered light. To quote Reference (9) "No satisfactory mathematical analysis of the light scattered or transmitted by a polydisperse cloud has been made. The distribution of sizes in a heterogeneous aerosol cannot be expressed in simple terms so that it is extremely difficult to apply the scattering functions for a homogeneous dispersion to the more complex system."

Diminution of the visibility of an object or its complete obscuration when viewed through a cloud is largely due to scattering phenomena, such as discussed above. This can be seen by considering the effect of scattering on the contrast ratio, a parameter which indicates the visibility of an object.

If we let B' = the brightness of an object O and
B'' = the brightness of the background surrounding O

Then the contrast, or contrast ratio, L is defined as

$$L = \frac{B' - B''}{B'}$$

When a cloud is interposed between the object and an observer there are two effects which reduce the contrast:

1. The light from the object and the background is attenuated due to scattering and, to a much lesser degree, due to absorption of the light by the scattering particles.

2. External light diffused from all directions is scattered by the cloud, some of it in the direction of the observer.

Let B_t' = the brightness of the object as seen through the cloud and

B_t'' = the brightness of the background as seen through the cloud

Then according to Reference (9)

$$B_t' = B' \cdot e^{\left(-K_S \pi r^2 n l\right)}$$

where K_S = the total scattering coefficient given in equation (5)

r = the particle radius

n = the number of particles per unit volume

l = the thickness of the cloud

Similarly $B_t'' = B'' \; e^{\left(-K_S \pi r^2 n l\right)}$

There will be a certain amount of scattered light or glare G, superimposed on both the brightness of the object and the background arising from the scattering of diffuse light by the cloud. Making the appropriate substitutions the new contrast L_t, as seen through the cloud is given by

$$L_t = \frac{(B' - B'')\, e^{\left(-K_S \pi r^2 n l\right)}}{B' e^{\left(-K_S \pi r^2 n l\right)} + G} \qquad (8)$$

When the attenuation and glare are great enough to reduce the contrast below a certain level, known as the "contrast threshold", then the object becomes indistinguishable. The value of the contrast threshold varies with the general light level and is somewhat dependent on the psychological and physiological factors of the observer. It has been

shown(10) that at observing brightness levels of about 4×10^{-3} foot lamberts, the contrast threshold is approximately 5%, while at lower light levels, e.g. 4×10^{-5} foot lamberts, a contrast of at least 30 - 40% is required for visibility. By "observing brightness" is meant the quantity in the denominator of Equation (8). It can be seen, therefore, that a contrast ratio such as 5% which is visible at a light level of 4×10^{-3} foot lamberts, would be obscured by a cloud, which reduces the light level below this value, since at lower light levels, higher contrast ratios are required. From another point of view, the above considerations mean that the smoke concentration required for obscuration will vary with the illumination level. The variation is a very slow one, however; according to Reference (10) the range of illumination level from moonlight to daylight increases the requisite smoke concentration by only a factor of two.

An impression of the brightness represented by a foot lambert may be obtained by reference to Table 2. Note that even white paper in moonlight is more than twice as bright as the greater of the two light levels mentioned above.

Table 2

BRIGHTNESS OF SOME EXTENDED SOURCES

Source	Brightness (footlamberts)
Surface of sun	6×10^8
Tungsten filament at 2700°K	3×10^6
White paper in sunlight	7300
Fluorescent lamp	1800
Candle flame	1500
Clear sky	930
Surface of moon	850
White paper in moonlight	0.009

NOTE: The numbers in the above Table were taken from Reference (11). The values were converted from units of candles/m^2 by using the definition:

$$\text{footlambert} = \frac{1}{\pi} \frac{\text{candle}}{\text{ft}^2}$$

which leads to the relation $\frac{\text{candle}}{\text{m}^2} = 0.292$ footlambert.

Interposing a cloud between an object and an observer, therefore, will decrease the contrast ratio because of the two effects discussed, which are summarized as follows:

1. The general light level is reduced and a contrast sufficient for visibility at the original light level may not be sufficient at the reduced light level.
2. The glare, since its final effect is to increase the denominator of the contrast ratio, will reduce the contrast, possibly below the threshold value.

A parameter often used to characterize a smoke is its optical density, defined as $\log_{10} (I_o/I)$, where I_o is the entrant intensity and I the emergent intensity of a parallel beam of light passed through the smoke. The attenuation is of course due to a combination of scattering and absorption effects. The scattering is by far the most important of these. In effect this measurement is a determination of the attenuation factor in the above Equation (8), $e^{\left(-K_S \pi r^2 n l\right)}$.

In making such measurements several precautions must be observed:

1. Since it has been estimated that half of the scattered light falls in a small cone of approximately 7° in the forward direction, precautions must be taken to accept and measure only the parallel component of the emergent beam. It is preferable also to use monochromatic light. Some workers prefer to make measurements at λ = 5240A which is qualitatively equivalent to white light and the light-adapted eye.

2. The optical density changes with time in a way which is dependent on the index of refraction, weight concentration per unit volume, and size distribution at any instant. If it is desired to compare different smokes, it is obvious that these parameters must be taken into account.

It should also be remembered that in making photometric measurements, it is often more practical and accurate to measure small differences at low light levels than at higher light levels. Thus a photocell would be able to detect a small amount of scattered light when that light is seen against an otherwise dark background; but if the photocell is exposed to a high level, the accuracy with which a small change in the light falling on the photocell can be determined is decreased. Therefore determination of the light scattered by a cloud or smoke, as measured against a black background, is a more sensitive method of evaluating the effect of the cloud or smoke, than direct determination of the attenuation of a light beam. It may not be a simple matter, however, to deduce the optical density from a measurement of scattered light.

Additional factors must be considered when one is concerned with a field problem(10). The distribution of smoke is seldom constant in the field. After its generation, the subsequent distribution of smoke is determined almost entirely by the diffusive properties of the atmosphere arising from the eddies in its turbulent motion. Diffusion in the molecular sense is negligible. Smoke concentration depends on smoke output, wind speed, and distance from the source as well as on atmospheric conditions.

4.2 Tests of Salted M1 and Salted and Unsalted T34 Propellants

Tests of the salted M1 (1.0% K_2SO_4) along with unsalted and salted (0.3% cryolite) T34 propellants were made in connection with the smoke obscuration problem in the 90 mm Gun M71E1 round of ammunition. Samples of these propellants were manufactured at Picatinny Arsenal in suitable granulations for the Caliber 0.50 weapon used in our tests. Data pertaining to these propellants are presented in Table 3.

Table 3

SPECIAL PROPELLANTS FOR SMOKE STUDIES

Propellant (Remarks) Lot	T34 (Salted) PA-E-28187	T34 (Unsalted) PA-E-28189	M1 (Salted) PA-E-28190
Composition			
Nitrocellulose, %	19.95	20.29	84.96
(%Nitrogen in Nitrocellulose), %	(12.6)	(12.6)	(13.15)
Nitroglycerin, %	19.03	19.00	-----
Nitroguanidine, %	54.69	54.55	-----
Dinitrotoluene, %	-----	-----	9.65
Dibutylphthalate, %	4.53	4.64	5.39
Diphenylamine (added), %	-----	-----	0.90
2-Nitrodiphenylamine, %	1.48	1.52	-----
Cryolite, %	0.32	-----	-----
Potassium Sulfate (added), %	-----	-----	0.90
Ethyl Alcohol (residual), %	0.03	0.05	0.27
Water (residual), %	0.00	0.00	0.10
Granulation			
Web, SP, grain, inches	0.0128	0.0119	0.0158
Calculated Thermochemical Properties			
Isochoric Flame Temperature, °K	2611	2607	2435
Force, ft-lbs/lb	333,750	334,460	303,330
Unoxidized Carbon, %	8.43	8.58	8.21
Heat of Explosion, cal/gm	807	809	701
Gas Volume, moles/gm	0.04594	0.04611	0.04477
Mean Heat Capacity, cal/gm/deg	0.3619	0.3627	0.3439

In our earlier smoke tests(3) we had used Ball M2 and Ball M33 copper jacketed projectiles. In the present tests we have used a special artillery type projectile with a 1/2 in. wide copper band ring seal. This projectile was originally designed for gun erosion tests at The Franklin Institute Laboratories and a considerable stock is still available. The type of projectile was changed in order to reduce the copper content of the smoke, which had averaged over 50% by weight in the tests with copper jacketed projectiles. It was thought that this would more accurately reproduce the type of gun smoke that is obtained in higher caliber weapons.

Propellant EX-5013-2 was tested with the artillery type projectiles for comparison with results obtained previously with this propellant using the copper jacketed projectiles.

The results of the firing tests are given in Table 4. The 266 gn. charge that was used with the EX-5013-2 propellant is the standard charge that was used in all our earlier tests with this propellant. The 180 gn. charge used for the salted and unsalted T34 propellants is the maximum weight that would fit into the cartridge cases. The 210 gn. charge for the M1 propellant did not quite fill the cases. A commercial (Staplex Co.) high volume air sampler, located behind the gun, was run for two minutes after each round to collect smoke particles on a filter of Dacron blanket material. The firing range was cleared of smoke with a large exhaust fan before firing each succeeding round. The smoke collected as determined by the increase in filter weight is a relative measure of the quantity of smoke produced. A smoke photometer was used to obtain a relative measure of optical density. As described in Reference (3) the observation involves use of a sensitive galvanometer to measure the output of a photoconductive cell which receives light scattered laterally by the smoke from a beam of approximately parallel light. If it can be assumed that the physical properties of the smokes tested do not vary greatly, then the galvanometer deflection can be taken as a relative indication of optical density.

Both the relative amounts of smoke collected and the smoke photometer readings indicate that the M1 smoke was considerably more dense than that from either of the T34 propellants. Practically all the rounds of these propellants resulted in a muzzle glow, but none produced the large, secondary type of flash. The muzzle glow from M1 propellant appeared to occupy a larger volume than the glow from the T34 propellants. These observations are qualitatively in agreement with those obtained at Aberdeen Proving Ground, where the M1 (1.0% K_2SO_4) and T34 (0.3% cryolite) propellants were tested in an M41 tube mounted in an M48A2 tank(12). It was observed that the M1 propellant produced "approximately twice as much smoke (slightly darker grey in color) as the T34. Both propellants are relatively flashless."

Table 4

RESULTS OF FIRING TESTS ON M1 AND T34 PROPELLANTS

Sample	Propellant	Lot No.	Charge (grains)	Smoke Collected in 20 Rounds (mg.)	Avg. Calv. Defl. on Smoke Photometer (mm)	Avg. Vel. (fps)	Rounds of Flash		
							Muzzle Glow	Secondary Flash	Other
31	M1 (salted, 1.0% K_2SO_4)	PA-E-28190	210	454	74	2600	20*		
32	T34 (unsalted)	PA-E-28189	180	159	20	2327	20		
33	T34 (salted, 0.3% cryolite)	PA-E-28187	180	172	30	2438	18		See Note 4
34	EX-5013-2 (unsalted)	AL-29422	266	468	16	2568		19	One round not observed
(20,25)*	" "	AL-29422	266	930	35	2540		19	One round not observed

Notes

1. Number of rounds fired: 20 for each propellant.
2. Weapon: Caliber 0.50 Browning Machine Gun.
3. Projectiles: 1/2 in. Bander Ring Seal Artillery Type (Originally designed for gun erosion tests at The Franklin Institute Laboratories), except in Samples 20 and 25, in which Ball M2 copper jacketed projectiles were used.
4. The first round in the test of Sample 33 had low velocity (2309 fps) and no flash; another round produced tongues of flame at the muzzle.

*Average for samples 20 and 25 reported in Reference (2).

•Volume of glowing gas was larger for Sample 31 than for Samples 32 and 33.

A comparison of the results for Samples 34 and (20, 25) in which unsalted EX-5013-2 propellant was fired with copper banded and copper jacketed projectiles, respectively, shows that both the quantity of smoke collected and the smoke density were cut approximately in half by changing the jacketed projectile to a non-jacketed one.

The quantity of smoke collected was in no case sufficient for chemical analysis by the procedures we had established when working with samples in which propellant and projectile contributed more smoke than in the present series of tests. Other filter materials were tested to see if the efficiency of smoke collection could be increased. One filter, manufactured by the Millipore Filter Corporation consisted of a thin cellulosic membrane with a closely spaced lattice of capillary pores of uniform (5.0μ) diameter. Although the pores became clogged after relatively little smoke was collected, the manufacturer's literature indicates that - compared to other filter materials - it should be easier to separate the smoke from the Millipore filter. Not only would a larger fraction of the smoke collected by recovered as a sample for analysis, but the sample would be less contaminated by filter material. Even so, it seemed that the quantity of sample would be so small as to require micro-analysis techniques. The development of such techniques is beyond the scope of the present investigation; but if it seems warranted, it may be possible to locate commercial houses already equipped to do such work.

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